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**Title:** Novel Browning Inhibitor Formulation for Fresh-Cut Apples

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# Novel Browning Inhibitor Formulation for Fresh-cut Apples

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ABSTRACT: Development of a browning inhibitor for fresh-cut apples that would not support human pathogen survival was investigated. Granny Smith and Fuji wedges were treated with acidic or neutral browning inhibitors with and without addition of sodium hexametaphosphate. Wedges in modified atmosphere packaging pouches were observed for browning during storage at 4 °C and 10 °C. A pH 2.9 dip containing ascorbic acid, citric acid, and sodium hexametaphosphate suppressed browning for at least 3 wk at 4 °C, whereas formulations without hexametaphosphate failed within 1 wk. These results demonstrate that browning in fresh-cut apples can be controlled with a formulation unlikely to support human pathogen survival or growth.

Keywords: fresh-cut, apples, browning inhibitors, hexametaphosphate, microbiological safety

### Introduction

n recent years, production of fresh-cut apples has increased dra-I matically, and further growth can be anticipated. This product is subject to enzymatic browning and must be treated with a browning inhibitor to prevent development of unsightly discoloration (Sapers and others 2002). Residual core tissues on fresh-cut apple and pear slices are more susceptible to browning than is parenchyma tissue, and the former defect usually limits product shelf-life (Brereton 1996; Sapers and Miller 1998). Browning-inhibitor formulations generally contain a reducing agent, such as ascorbic acid, and also may contain other browning inhibitors or adjuncts, such as citric acid, a calcium salt, cysteine, polyphosphates, or 4-hexylresorcinol (Sapers 1993; Sapers and others 2002). Such formulations may be acidic or neutral in pH; one of the most widely used browning inhibitors is a neutral product containing calcium ascorbate, marketed as NatureSeal™ (Chen and others 1999; Chen and others 2000).

Fresh-cut apples as well as other fresh-cut fruits and vegetables do not receive a "kill" step and so may contain viable microorganisms including human pathogens. The potential for human pathogen contamination is indicated by numerous outbreaks of Escherichia coli O157:H7 food poisoning associated with unpasteurized apple cider (NACMCF 1999). Escherichia coli (generic) is found in the orchard environment, may be detected on fresh apples (Riordan and others 2001), and can grow in wounds on the apple surface (Janisiewicz and others 1999; Sapers and others 2000; Gunes and Hotchkiss 2002), creating opportunities for preharvest contamination. Postharvest contamination with Listeria monocytogenes in the packing or fresh-cut processing plant environment represents another microbial hazard. Detection of L. monocytogenes in freshcut apples (USFDA 2001a) and red bell peppers (USFDA 2001b) resulted in product recalls in 2001. Survival and growth of L. monocytogenes on apple slices was demonstrated by Conway and others (2000). Preliminary studies in our laboratory indicated that Listeria

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innocua was able to survive and grow in a chilled, neutral pH browning inhibitor solution similar to that widely used by fresh-cut apple processors (Karaibrahimoglu and others 2004). Use of an acidic formulation probably would have suppressed survival and growth of *L. monocytogenes* in the dip, thereby preventing crosscontamination of the fresh-cut product.

Our objective was to develop an acidic browning-inhibitor formulation that could prevent discoloration of the cut surface and residual core tissue on fresh-cut apple slices without inducing tissue breakdown during product storage.

### **Materials and Methods**

## Raw material source and fresh-cut processing

Granny Smith and Fuji apples were purchased at local supermarkets and stored at 4 °C for 1 to 11 d before use in processing experiments carried out between June and September 2000. Depending on availability, the fruit originated in Southern Hemisphere production locations during the 2000 growing season and presumably was in controlled atmosphere (CA) storage for 2 to 4 mo before purchase or was produced in Washington State during the 1999 season and held in CA storage for 9 to 11 mo before purchase.

The apples were sanitized by immersion for 2 min in 1000 mg/L Cl2 solution (total Cl2 calculated from level of added sodium hypochlorite, adjusted to pH 6.5 with citric acid) and rinsed with tap water before fresh-cut processing. The apple stem and calyx ends were removed by cutting perpendicular to the apple axis with a knife. Then, the apples were cut with a Westmark wedger/corer (Westmark Divisorex, Herscheid, Germany), which makes 10 wedges and removes a 22-mm-dia core. Because this size corer was insufficient to remove most of the core tissue from Fuji apples, which have a larger core than Granny Smith, the former variety was cored with a 31-mm-dia stainless-steel cutting tube before cutting of wedges. To minimize browning during sample preparation, the wedges from individual apples were immersed in browning inhibitor solution for 2 min immediately after cutting, removed with a colander, and pooled until sufficient wedges were accumulated to meet requirements of the experimental design (each sample containing the wedges from 8 apples). In some experiments, the dipped wedges were placed in a colander and rinsed by spraying with tap

Table 1 - pH of Browning-inhibitor formulations

| Formulation <sup>a</sup>                           | рH  |
|--|-----|
| 2% Na erythorbate + 0.1% CaCl <sub>2</sub>         | 7.6 |
| 2% AA + 1% CA + 0.2% CaCl, *                       | 2.2 |
| 2% AA + 1% CA + 0.5% Na HMP                        | 2.5 |
| 2% AA + 1% CA + 1% Na HMP                          | 2.6 |
| 2% AA + 1% CA + 2% Na HMP                          | 2.8 |
| 2% AA + 1% CA + 0.2% CaCl <sub>2</sub> + 1% Na HMP | 2.5 |
| 2% AA + 1% CA + 1% Na HMP + 0.2% NaCl              | 2.6 |
| 2% AA + 1% CA + 1% Na HMP + 0.5% NaCl              | 2.5 |
| 3% AA + 1% CA + 0.5% Na HMP                        | 2.4 |
| 3% AA + 1% CA + 1% Na HMP                          | 2.6 |
| 3% AA + 1% CA + 2% Na HMP                          | 2.8 |
| 3% AA + 1% CA + 1% Na HMP + 0.2% NaCl              | 2.5 |
| 3% AA + 1% CA + 1% Na HMP + 0.5% NaCl              | 2.5 |

\*AA = ascorbic acid; CA = citric acid; HMP = hexametaphosphate.

water (60 mL per 454 g apple wedges) with an HDPE/Nylon Industrial Spray Bottle, 480 mL (Cole-Palmer, Vernon Hills, Ill., U.S.A.) held 20 to 25 cm from the wedges; during rinsing the wedges were flipped over once to ensure coverage of both sides. The pooled wedges were de-watered by spinning for 10 revolutions in a salad spinner (Copco Model 604, Wilton Industries Co., Woodbridge, Ill., U.S.A.). Each treated sample was distributed into 8 Cryovac (Cryovac Div., Sealed Air Corp., Rochester, N.Y., U.S.A.) film pouches (laminated polyethylene with OTR of 1395 cc/m²/d), each holding 8 to 10 wedges weighing 108 to 120 g, and the pouches were then heat-sealed. Samples were stored at 4 °C and 10 °C for up to 3 wk.

### **Browning-inhibitor formulations**

Browning-inhibitor solutions were prepared from the following chemicals: citric acid monohydrate (CA, Mallinckrodt Baker Inc., Paris, Ky., U.S.A.), sodium erythorbate (97%; Aldrich Chemical Co., Milwaukee, Wis., U.S.A.), calcium chloride dihydrate (CaCl<sub>2</sub>, J.T. Baker Chemical Co., Phillipsburg, N.J., U.S.A.), ascorbic acid (AA, Aldrich Chemical Co.), sodium hexametaphosphate (Na HMP, Hexaphos; Astaris, St. Louis, Mo., U.S.A.), and sodium chloride (Morton Intl. Inc., Chicago, Ill., U.S.A.). Browning inhibitor solutions were prepared with tap water. The pH of each formulation was determined with a Beckman Model 360 pH Meter (Beckman Coulter Inc., Fullerton, Calif., U.S.A.) and a Beckman Futura Model 511084 combination pH electrode (Beckman Coulter Inc.) with stirring. The formulations compared in this study are listed in Table 1.

### Sample evaluation

Because browning of treated samples during storage occurred in residual seed pocket areas and other core tissue before browning of the sides of fresh-cut wedges and would limit product shelf-life, we evaluated browning of the former tissues. However, we were unable to use a spectrocolorimeter or tristimulus colorimeter, as had been done in earlier studies (Sapers and Douglas 1987; Sapers and Miller 1998) because of the irregular surface and small size of discolored areas relative to the aperture size of our instrumentation. Instead, samples were observed visually for the onset of core tissue browning at intervals during storage by the 2 authors and a food scientist employed by the cooperating company, all observers having had extensive experience in evaluating fresh-cut apples. Samples were coded by the senior author and presented to the other 2 observers without disclosing sample identity. The onset of browning was defined as the day when 2 or more wedges of the 32 to 40 wedges within a 4-pouch sample were judged by the observers to have a moderate or severe degree of core browning. This criterion was se-

Table 2—Effect of alternative browning inhibitor formulations on control of core browning in fresh-cut Granny Smith apples

|          |   | Onset of core browning <sup>c</sup> (d) |                 |
|----------|---|---|-----------------|
| Experime | xperiment <sup>a</sup> Treatment <sup>b</sup> |   | 10 °C           |
| A        | 2% Na erythorbate + 0.1% CaCl <sub>2</sub>    | 1                                       | 1               |
|          | 2% AA + 1% CA + 0.2% CaCl,                    | >14                                     | 4               |
|          | 2% AA + 1% CA + 1% Na HMP                     | >21                                     | >21             |
| В        | 2% AA + 1% CA + 0.2% CaCl,                    | 2                                       | 1               |
|          | 2% AA + 1% CA + 1% Na HMP                     | 26                                      | 26              |
|          | 2% AA + 1% CA + 1% Na HMP +                   |   |                 |
|          | 0.2% CaCl <sub>2</sub>                        | >26                                     | >26             |
|          | 3% AA + 1% CA + 1% Na HMP                     | >26                                     | 19              |
| С        | 2% AA + 1% CA + 1% Na HMP                     | >24                                     | 20 <sup>d</sup> |
|          | 2% AA + 1% CA + 0.5% Na HMP                   | >24                                     | 24 <sup>d</sup> |
| D        | 2% Na erythorbate + 0.1% CaCl <sub>2</sub>    | 1                                       | 1               |
|          | 2% AA + 1% CA + 0.2% CaCl, *                  | 9                                       | 6               |
|          | 2% AA + 1% CA + 0.5% Na HMP                   | 13                                      | 6               |

Experiments performed during summer of 2000: A apples from 2000 season, Chile; B, C, and D apples from 1999 season, Washington, USA.

b22-mm-dia core removed during preparation of wedges; AA = ascorbic acid; CA = citric acid; HMP = hexametaphosphate; 2 min dip.

First day when moderate or severe core browning observed on at least 2 wedges within sample, which comprised 4 bags, each containing 8 to 10 wedges.

Indeterminate due to severe tissue breakdown.

lected on the basis of the conspicuous nature of wedges with core browning, which would render a pouch containing even a few such wedges unattractive to consumers. Additional observations were made of the onset of tissue breakdown in the stored wedges, which was manifested by the development of a waterlogged and dark appearance.

### Results and Discussion

Preliminary studies conducted by the authors indicated that neutral browning-inhibitor formulations tended to be less effective than acidic formulations in controlling core browning but avoided damage to apple tissue induced by the acidic treatment (Pilizota and Sapers 2000). These studies also showed that addition of Na HMP to an acidic browning-inhibitor treatment suppressed core browning. Addition of the polyphosphate to a neutral formulation was less effective. In some trials with Na HMP addition, tissue breakdown was observed in treated wedges.

In this study, we investigated the effectiveness of Na HMP addition to an acidic browning-inhibitor formulation in delaying core browning in fresh-cut Granny Smith and Fuji apples. Browning of the cut wedge surface other than the core area was not shelf-lifelimiting in this study. Results with Granny Smith (Table 2) indicated that treatment with the neutral (2% Na erythorbate + 0.1% CaCl<sub>2</sub>) browning-inhibitor formulation was unable to suppress core browning even for 1 d at 4 °C or 10 °C (experiments A and D). The acidic formulation (2% AA + 1% CA + 0.2% CaCl<sub>2</sub>) gave somewhat better but highly variable results (experiments A, B, and D). However, addition of 1% Na HMP to an acidic formulation containing 2% AA and 1% CA suppressed core browning for at least 2 wk and in several trials for more than 3 wk, at 4 °C. Generally, similar results were obtained at 10 °C. Further improvement in control of core browning resulted from addition of 0.2% CaCl2 to the 1% Na HMP formulation (experiment B). Differences in raw material ripeness and storage history may be responsible for variability in treatment response. Increasing the AA concentration from 2% to 3% did not appear to improve browning inhibitor performance.

With Fuji apples, neither the acidic nor the neutral browning-inhibitor formulation was able to suppress core browning (Table 3).

Table 3 — Effect of alternative browning inhibitor formulations on control of core browning in fresh-cut Fuji apples

| Experime | nt <sup>a</sup> Treatment <sup>b</sup>     | 4 °C  | 10 °C           |
|----------|--|-------|-----------------|
| E        | 2% Na erythorbate + 0.1% CaCl <sub>2</sub> | 1     | 1               |
| _        | 2% AA + 1% CA + 0.2% CaCl,                 | 1     | 1               |
|          | 2% AA + 1% CA + 1% Na HMP                  | 1     | 1               |
|          | 2% AA + 1% CA + 2% Na HMP                  | 1     | 1               |
|          | 3% AA + 1% CA + 1% Na HMP                  | 18    | 18              |
|          | 3% AA + 1% CA + 2% Na HMP                  | >18   | >18             |
| F        | 3% AA + 1% CA + 1% Na HMP                  | >21   | 16 <sup>d</sup> |
| Ġ        | 2% AA + 1% CA + 1% Na HMP                  | 18-21 | 22 <sup>d</sup> |
| •        | 3% AA + 1% CA + 1% Na HMP                  | >22   | 22 <sup>d</sup> |
| н        | 2% AA + 1% CA + 1% Na HMP                  | >21   | 21 <sup>d</sup> |
| •••      | 3% AA + 1% CA + 1% Na HMP                  | >21   | >21             |
|          | 3% AA + 1% CA + 0.5% Na HMP                | >21   | >21             |
| 1        | 2% AA + 1% CA + 1% Na HMP +                |       |                 |
| •        | 0.2% NaCl                                  | 5     | 5               |
|          | 2% AA + 1% CA + 1% Na HMP +                | -     |                 |
|          | 0.5% NaCl                                  | 3     | 1               |
|          | 3% AA + 1% CA + 1% Na HMP +                | -     |                 |
|          | 0.2% NaCl                                  | 14    | 10              |
|          | 3% AA + 1% CA + 1% Na HMP +                | ••    |                 |
|          | 0.5% NaCl                                  | 14    | 14              |

aExperiments performed during summer of 2000: E apples from 2000 season, South Africa; F, G, H, and I apples from 2000 season, New Zealand. b31-mm-dia core removed during preparation of wedges; AA = ascorbic acid;

CA = citric acid; HMP = hexametaphosphate; 2 min dip. First day when moderate or severe core browning observed on at least 2 wedges within sample, which comprised 4 bags, each containing 8 to 10 wedges.

dindeterminate due to severe tissue breakdown

The Na HMP formulation used successfully with Granny Smith apples gave inconsistent results with Fuji (experiments E and I). Increasing the Na HMP concentration in the dip from 1% to 2% or addition of 0.2% or 0.5% NaCl to the browning inhibitor did not improve treatment efficacy. However, increasing the AA concentration from 2% to 3% consistently suppressed core browning for 2 to 3 wk at 4 °C. This treatment yielded similar results during storage at 10 °C. Additional study would be required to establish how much of the improvement in shelf-life could be realized by 3% AA without Na HMP, whether synergism between AA and HMP was involved, or whether further improvements could be obtained by greater increases in AA concentration.

Commercial application of browning inhibitor dips may require a posttreatment rinse to remove excess browning inhibitor solution so that the treatment chemicals can be considered as processing aids. In this study, a posttreatment rinse with water had little or no effect on the efficacy of the acidic Na HMP treatment in suppressing core browning (Table 4). Presumably, there was sufficient residual AA, CA, and Na HMP, even after rinsing, to suppress core tissue browning. Thus, such a treatment might not qualify as a processing aid.

In some experiments, treatment with dips containing Na HMP did induce tissue breakdown (Table 5). This defect occurred with both apple varieties, but only at 10 °C and was usually coincident with the onset of core browning. Tissue breakdown in Granny Smith samples appears to have been suppressed by addition of 0.2%  $\rm CaCl_2$  to the browning inhibitor (experiment B). Whether tissue breakdown represents a problem under some treatment conditions or is related to raw material quality deficiencies should be investigated.

No formal sensory evaluations of the treated apple slices were carried out in this study. However, some Granny Smith samples were found to be sour, perhaps because of the high acidity of the

Table 4—Effect of posttreatment rinsing on control of core browning by novel browning-inhibitor formulations containing sodium hexametaphosphate

|              |                           |       | Onset of core<br>browning <sup>c</sup> (d) |       |
|--------------|---------------------------|-------|--|-------|
| Variety*     | Treatmentb                | Rinse | se 4 °C 10 °C                              | 10 °C |
| Granny Smith | 2% AA + 1% CA + 1% Na HMP | No    | >17  | >17   |
|              |                           | Yes   | >16  | >16   |
| Fuji         | 3% AA + 1% CA + 1% Na HMP | No    | >17  | >17   |
|              |                           | Yes   | 16   | 16    |

aGranny Smith apples from California, 2000 season; Fuji apples from Chile, 2000 season.

bSee Table 2 and 3 footnotes for treatments.

First day when moderate or severe core browning observed on at least 2 wedges within sample, which comprised 4 bags, each containing 8 to 10 wedges.

Table 5 — Onset of tissue breakdown in fresh-cut apples treated with alternative browning-inhibitor formulations

| Variatu                            |  | Onset of tissue<br>breakdown <sup>c</sup> (d) |       |
|------------------------------------|--|---|-------|
| Variety<br>Experiment <sup>a</sup> | Treatmentb                             | 4 °C  | 10 °C |
| Granny Smith                       |  |   |       |
| В                                  | 2% AA + 1% CA + 0.2% CaCl <sub>2</sub> | >26   | >26   |
| _                                  | 2% AA + 1% CA + 1% Na HMP              | >26   | 26    |
|                                    | 2% AA + 1% CA + 1% Na HMP              | +   |       |
|                                    | 0.2% CaCl <sub>a</sub>                 | >26   | >26   |
|                                    | 3% AA + 1% CA + 1% Na HMP              | >26   | 21    |
| С                                  | 2% AA + 1% CA + 1% Na HMP              | >24   | 20    |
| •                                  | 2% AA + 1% CA + 0.5% Na HM             | P >24   | 24    |
| Fuji                               |  |   |       |
| F                                  | 3% AA + 1% CA + 1% Na HMP              | >21   | 16    |
| G                                  | 2% AA + 1% CA + 1% Na HMP              | >22   | 22    |
| <del>-</del> -                     | 3% AA + 1% CA + 1% Na HMP              | >22   | 22    |
| н                                  | 2% AA + 1% CA + 1% Na HMP              | >21   | 21    |
| • •                                | 3% AA + 1% CA + 1% Na HMP              | >21   | >21   |
|                                    | 3% AA + 1% CA + 0.5% Na HM             | P >21   | >21   |

Experiments performed during summer of 2000: See Table 1 and 2 footnotes for origin of samples.

origin of samples.
See Table 2 and 3 tootnotes for treatments.

CFirst day when breakdown observed on at least 2 wedges within sample, which comprised 4 bags, each containing 8 to 10 wedges.

raw material, and samples of both varieties developed a pineapplelike aroma during prolonged storage at 10 °C. We suspect that the latter defect was related to declining oxygen concentrations within the sealed pouches, possibly bringing about a shift to anaerobic respiration with concomitant production of ethanol and ethyl esters. The importance of these observations should be confirmed in further studies.

Phosphates have been used previously as components of browning-inhibitor formulations. An unspecified "food-grade phosphate" was combined with citric acid and dextrose in a product called Salad Fresh<sup>TM</sup> (Ingredient Technology Corp., Elyria, Ohio, U.S.A.), which was recommended for maintaining the appearance and freshness of various fruits and vegetables (Duxbury 1986). We reported that a highly acidic glassy polyphosphate (Sporix; Intl. Sourcing Inc., South Ridgewood, N.J., U.S.A.) was effective in controlling browning of apples and apple juice (Sapers and others 1989). A browning-inhibitor formulation produced by Monsanto (Snow Fresh<sup>TM</sup>, Monsanto Chemical Co., St. Louis, Mo, U.S.A.) was a blend of sodium acid pyrophosphate with ascorbic acid, citric acid, and calcium chloride (Duxbury 1988). The Monsanto patent claims call for use of an alkali metal acid polyphosphate salt, more

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specifically, sodium acid pyrophosphate (Warren 1991). However, to our knowledge, no one has reported on use of Na HMP, a neutral polyphosphate (Dziezak 1990), in a browning-inhibitor formulation. Presumably, HMP acts as a sequestrant of copper in polyphenol oxidase, thereby inhibiting this enzyme and suppressing browning (Mayer and Harel 1979).

### Conclusions

ur results demonstrate the efficacy of an acidic browninginhibitor formulation containing HMP in suppressing shelflife limiting core tissue browning in fresh-cut apples. The low pH of this dip (2.9) is unlikely to support long-term survival or growth of Listeria in the browning inhibitor solution, even under extended use conditions (Parish and Higgins 1989; Ita and Hutkins 1991). Thus, a potential source of product contamination can be eliminated by use of this novel browning-inhibitor formulation.

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Mention of brand or firm names does not constitute an endorsement by the U.S. Dept. of Agriculture over others of a similar nature not mentioned.

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